OCR
RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS
Advanced GCE

CHEMISTRY (SALTERS)

Chemistry by Design

2854

Tuesday **29 JUNE 2004** Morning 2 hours

Candidates answer on the question paper
Additional materials:
Data Sheet for Chemistry (Salters)
Scientific Calculator

Candidate Name	

Centre Number						Candidate Number				

TIME 2 hours

INSTRUCTIONS TO CANDIDATES

- Write your name, Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
  DO NOT ANSWER IN PENCIL. **DO NOT** WRITE IN THE BARCODE. **DO NOT** WRITE IN THE GREY AREAS BETWEEN THE PAGES.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [ ] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use a *Data Sheet for Chemistry (Salters)*.
- You are advised to show all the steps in calculations.

FOR EXAMINER'S USE		
Qu.	**Max.**	**Mark**
1	**32**	
2	**26**	
3	**18**	
4	**31**	
5	**13**	
TOTAL	**120**	

This question paper consists of 15 printed pages and 1 blank page.

Registered Charity Number: 1066969
[Turn over

Answer **all** the questions.

For Examiner's Use

1 Nitric acid is made from ammonia by the Ostwald process.

The ammonia is converted to nitrogen monoxide, NO, which is then reacted with air.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = -115\,kJ\,mol^{-1} \qquad \textbf{equation 1.1}$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -58\,kJ\,mol^{-1} \qquad \textbf{equation 1.2}$$

The N_2O_4 is then dissolved in water. The overall reaction is shown below.

$$3N_2O_4(g) + 2H_2O(g) \rightleftharpoons 4HNO_3(aq) + 2NO\,(g) \qquad \Delta H = -103\,kJ\,mol^{-1} \qquad \textbf{equation 1.3}$$

(a) (i) Give the name of the substance NO_2.

.....[1]

(ii) Suggest **one** use for the nitric acid that is made in this process.

.....[1]

(b) Give the oxidation states of nitrogen in the compounds shown below.

NH_3 ..... N_2O_4 ..... HNO_3 ..... [3]

(c) Look at **equation 1.1**. Explain the effect of increasing the temperature on the rate of the reaction and the yield of NO_2.

(i) Explain the effect of increasing the temperature on the **rate of reaction**.

.....

.....

.....

.....

.....[3]

(ii) Explain the effect of increasing the temperature on the **yield** of NO_2.

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.....[3]

(d) In view of your answers to **(c)(i)** and **(ii)**, suggest why a temperature of 25 °C is used for the reaction in **equation 1.1**.

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.....[2]

(e) **(i)** Write an expression for the equilibrium constant, K_p, for the reaction in **equation 1.2**.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -58\ kJ\ mol^{-1} \qquad \textbf{equation 1.2}$$

K_p =

[2]

(ii) Give the units of K_p when partial pressures are measured in atmospheres.

units of K_p .....
[1]

(iii) At 25 °C, K_p has a numerical value of 8.7. Calculate the partial pressure of $N_2O_4(g)$ in an equilibrium mixture where the partial pressure of $NO_2(g)$ is 0.60 atm. Give your answer to a suitable number of significant figures.

partial pressure of N_2O_4 = ...atm [2]

(f) N_2O_4 is an acidic oxide of an element in Period 2. Suggest **two** other elements in this period that form acidic oxides.

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.....[2]

(g) **(i)** The NO(g) formed in **equation 1.3** must not be allowed to escape into the atmosphere, as it is a pollutant.
Give **two** harmful effects of this gas.

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.....[2]

(ii) Suggest what happens to the NO(g) formed in the industrial process.

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.....[1]

[Turn over

(h) For the forward reaction in **equation 1.2**, deduce the **signs** of the following entropy changes, giving your reasons.

For Examiner's Use

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -58\ kJ\ mol^{-1} \qquad \textbf{equation 1.2}$$

(i) ΔS_{sys} .....

.....[1]

(ii) ΔS_{surr} .....

.....[1]

(iii) ΔS_{total} .....

.....

.....[2]

(i) Nitric acid, HNO_3, is a strong acid in aqueous solution.

(i) Explain what is meant by the term *strong* acid.

.....

.....[1]

(ii) Write a chemical equation for the reaction that occurs when HNO_3 dissolves in water.

[2]

(iii) Calculate the pH of a 0.050 mol dm^{-3} solution of nitric acid.

pH = ...[2]

[Total: 32]

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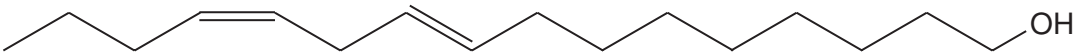
2 Some female moths can attract male moths from great distances by emitting minute quantities of a substance called a pheromone. The formula of one such pheromone is shown below.

For Examiner's Use



(a) Name **two** different functional groups in the pheromone structure.

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.....[2]

(b) In this question, two marks are available for the quality of the use and organisation of scientific terms.

Initial analysis of the structure of the pheromone was done using spectroscopy. Describe how **infrared spectroscopy** and **mass spectrometry** could be used to help to identify the pheromone structure.

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.....[5]

Quality of Written Communication [2]

(c) After spectroscopy, chemical reactions were used to continue the analysis. When the pheromone is distilled with acidified potassium dichromate(VI), partial oxidation occurs to give an aldehyde group.

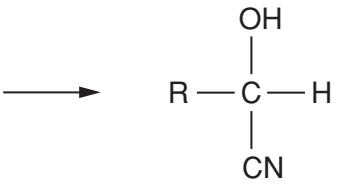
(i) Draw the **full structural** formula of the aldehyde group –CHO.

[1]

For Examiner's Use

(ii) When an aldehyde RCHO reacts with HCN, a compound **Q** is formed.

Draw diagrams to illustrate the **mechanism** of the attack of CN^- on the aldehyde RCHO, followed by the attack of an H^+ ion on the intermediate to give compound **Q**.



compound **Q**

[3]

(d) A technique called ozonolysis breaks the pheromone molecule at its double bonds. The carbon atoms on either side of the break are oxidised to carboxylic acid groups. The smallest molecule produced is HOOC—CH_2—COOH, propanedioic acid.

(i) Propanedioic acid can be detected by its n.m.r. spectrum. Give the number of peaks you would expect in this n.m.r. spectrum and their relative areas.

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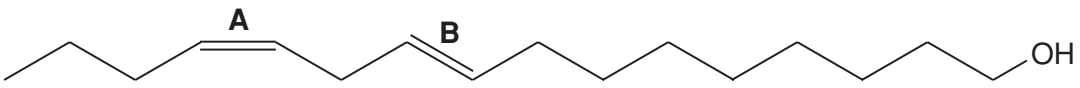
.....[2]

(ii) Give the formula of another molecule that would be produced as a result of ozonolysis of the pheromone. [2]

(e)



The shape of the pheromone molecule is affected by its two double bonds that have different arrangements of the groups around them. Name the **type** of geometric isomerism shown at double bonds **A** and **B** in the structure above.

A .....

B .....[2]

(f) Suggest how the male moth detects the pheromone on a molecular level. Say why the shape of the pheromone molecule is important in this process.

For Examiner's Use

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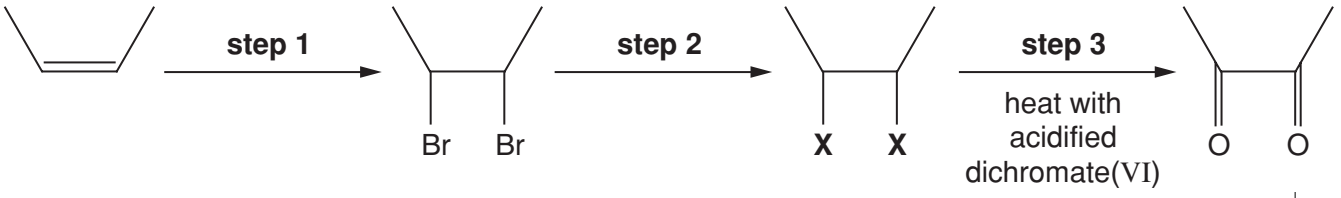
.....[3]

(g) A chemist set out to synthesise a new compound from the pheromone.

This involved the following synthetic route.



(i) Suggest a reagent for **step 1** .....[1]

(ii) Suggest the identity of the functional group **X** .....[1]

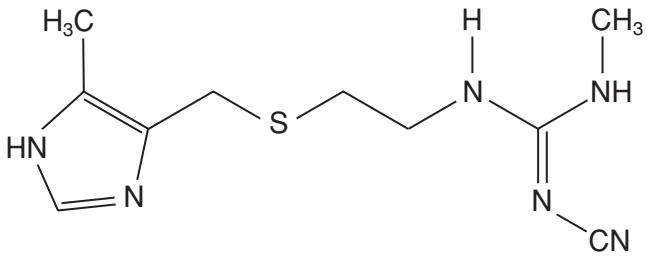
(iii) Give the reagent and conditions for **step 2**.....

.....[2]

[Total: 26]

3 The compound cimetidine is an effective anti-ulcer medicine that works by decreasing acid secretion in the stomach. It was one of the first medicines to be designed logically from first principles, based on an understanding of the chemical processes that take place in the body.

For Examiner's Use



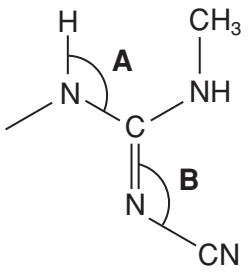
cimetidine

(a) (i) Work out from the formula the number of carbon and hydrogen atoms in a molecule of cimetidine.

carbon atoms .....

hydrogen atoms .....[2]

(ii) Suggest values for the bond angles **A** and **B** in the part of the cimetidine molecule shown below.

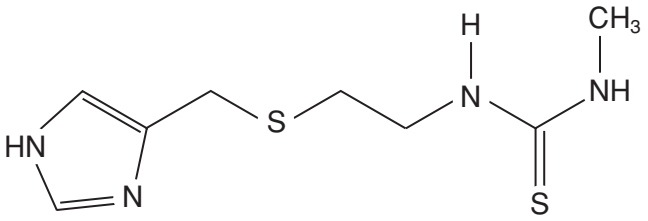


A ..... **B** ..... [2]

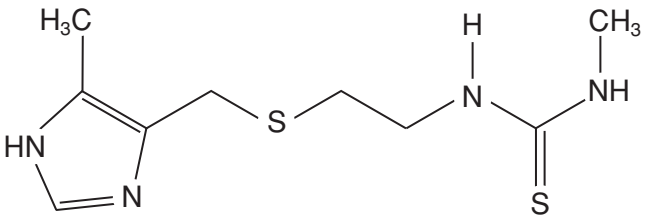
[Turn over

(b) As part of the development, **compound A** was synthesised and this showed anti-ulcer activity. **Compound A** was not entirely satisfactory, however, so further development produced metiamide.

For Examiner's Use



compound A



metiamide

Suggest why early versions of pharmaceutical products are not always 'entirely satisfactory'.

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.....[1]

(c) The ring structure in the two compounds above shows aromatic character, similar to that in benzene.

(i) Benzene has delocalised electrons. Explain how *delocalisation* occurs in the benzene ring, giving **one** important consequence.

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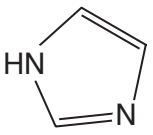
(ii) Suggest reagents and conditions for making metiamide from **compound A**.

Assume the ring 

behaves like benzene.

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.....[3]

(iii) Circle a word in the list below that describes the substitution reactions of benzene.

For Examiner's Use

nucleophilic **electrophilic** **radical** [1]

(iv) Some compounds with delocalised electrons (like **compound A**, metiamide and benzene) are colourless.
Other substances with delocalised electrons (like dyes) are coloured.

Explain, in terms of transitions between electronic energy levels, why some compounds with delocalised electrons are coloured while others are colourless.

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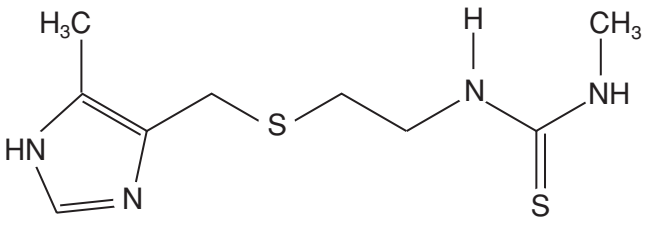
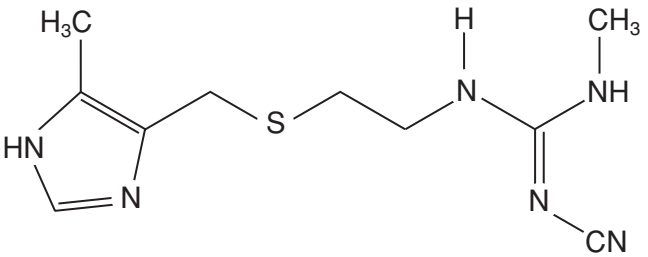
.....[4]

(d) Metiamide still caused a few problems in trials, so its structure was modified to cimetidine which has the same pharmacophore as metiamide but works better.



metiamide



cimetidine

Draw a ring round the pharmacophore on the **cimetidine** structure. [1]

[Total: 18]

[Turn over

4 Farmers add slaked lime, calcium hydroxide, to their fields to neutralise the acidity of clay soils. Slaked lime is produced from limestone, $CaCO_3$. The limestone is first heated to form calcium oxide, CaO. A controlled amount of water is then added to the calcium oxide to produce solid slaked lime.

For Examiner's Use

(a) (i) Write a balanced chemical equation for the action of heat on calcium carbonate.

[1]

(ii) Calculate the mass of calcium oxide made by complete decomposition of 1.0 kg of calcium carbonate.

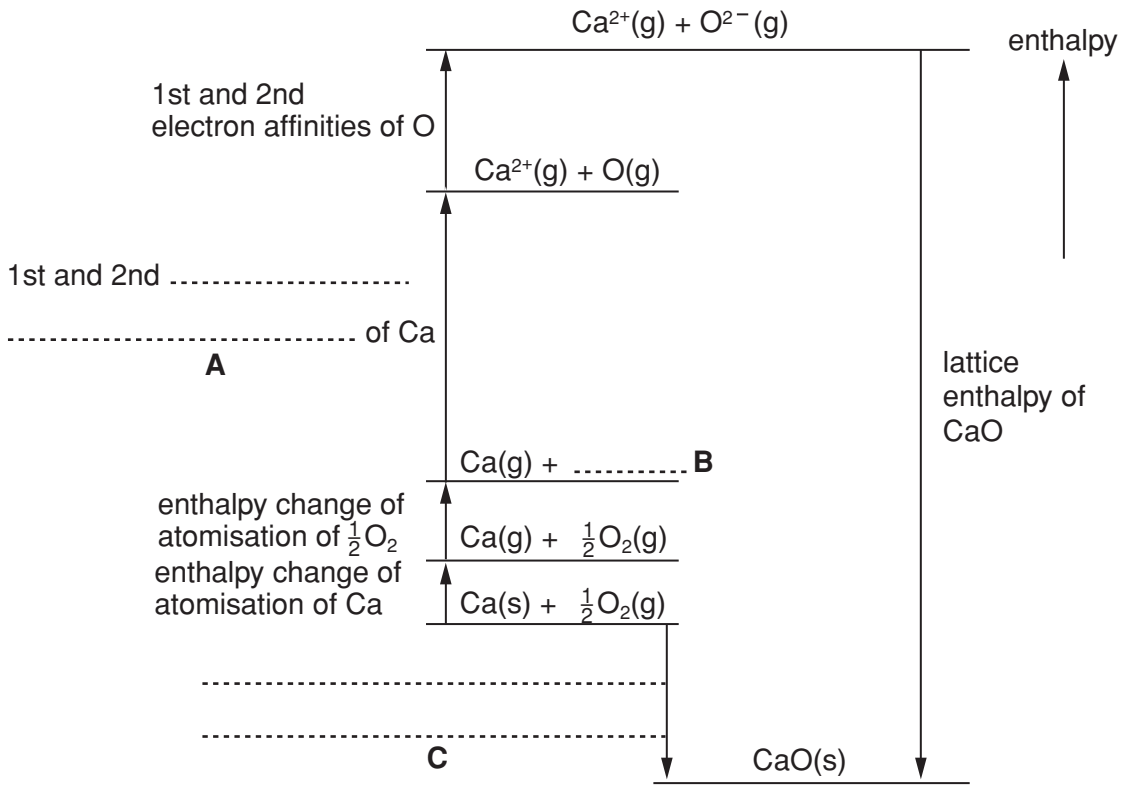
A_r: Ca, 40; C,12; O,16

mass = ...g [2]

(b) Draw a dot-cross diagram to show the ions present in calcium oxide, CaO.

[2]

(c) (i) A Born-Haber cycle for calcium oxide is shown. Complete the cycle by writing suitable labels on the dotted lines at points **A**, **B** and **C**.



[3]

(ii) Use the data in the table and the cycle in **(i)** to calculate a value for the sum of the first and second electron affinities of O(g). **Give a sign with your answer.**

For Examiner's Use

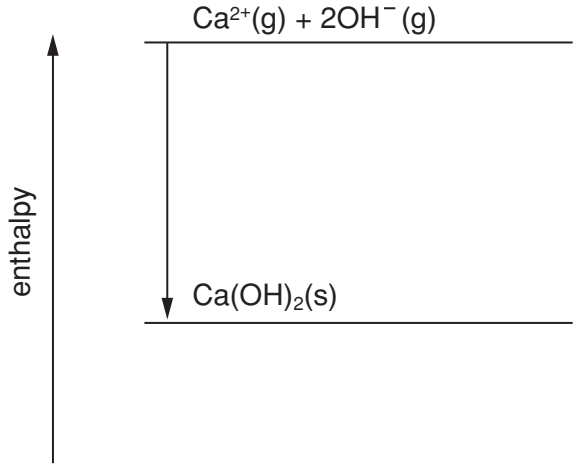
enthalpy change	value/ kJ mol^{-1}
A	+1748
C	–635
lattice enthalpy of CaO(s)	–3419
atomisation of Ca(s)	+178
atomisation of $\frac{1}{2}O_2$(g)	+249

sum of first and second electron affinities of O(g) = ...kJ mol^{-1} [3]

(d) Calcium hydroxide, $Ca(OH)_2$, is formed by the reaction of calcium oxide with water. Calcium hydroxide is only slightly soluble in water. One reason for this is its positive enthalpy change of solution in water.

(i) Part of an enthalpy level diagram to show the dissolving of calcium hydroxide in water is given. Complete the diagram by following the instructions below.

- Draw an appropriate enthalpy level for aqueous calcium hydroxide and label it.
- Label the enthalpy change that is shown by the arrow on the diagram.
- Draw in and label the remaining enthalpy changes involved in the cycle.



[4]

(ii) Describe the trend of solubilities in the Group 2 hydroxides.

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.....[1]

[Turn over

(e) The solubility of calcium hydroxide in water is 0.016 mol dm^{-3} at 298 K.

For Examiner's Use

(i) Calculate the concentration of hydroxide ions in a saturated solution of calcium hydroxide, $Ca(OH)_2$, at 298 K, assuming that it is a strong base.

$[OH^-]$ = ...mol dm^{-3} [2]

(ii) $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 298 K.
Calculate the pH of a saturated solution of calcium hydroxide at this temperature.

pH = ...[3]

(iii) Write a balanced equation for the reaction of calcium hydroxide with hydrochloric acid.

[2]

(iv) Calculate the volume of 0.0200 mol dm^{-3} hydrochloric acid which would react exactly with 10.0 cm^3 of 0.0150 mol dm^{-3} calcium hydroxide.

volume = ...cm^3 [2]

(f) In this question, one mark is available for the quality of spelling, punctuation and grammar.

As the H^+ ions in the soil solution are neutralised by the OH^- ions in the slaked lime, they are replaced by the H^+ ions adsorbed on the surface of the clay. The calcium ions take the place of the H^+ ions in the clay.

Explain how H^+ ions are held in clay soils and how they are displaced by calcium ions.

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.....[5]

Quality of Written Communication [1]

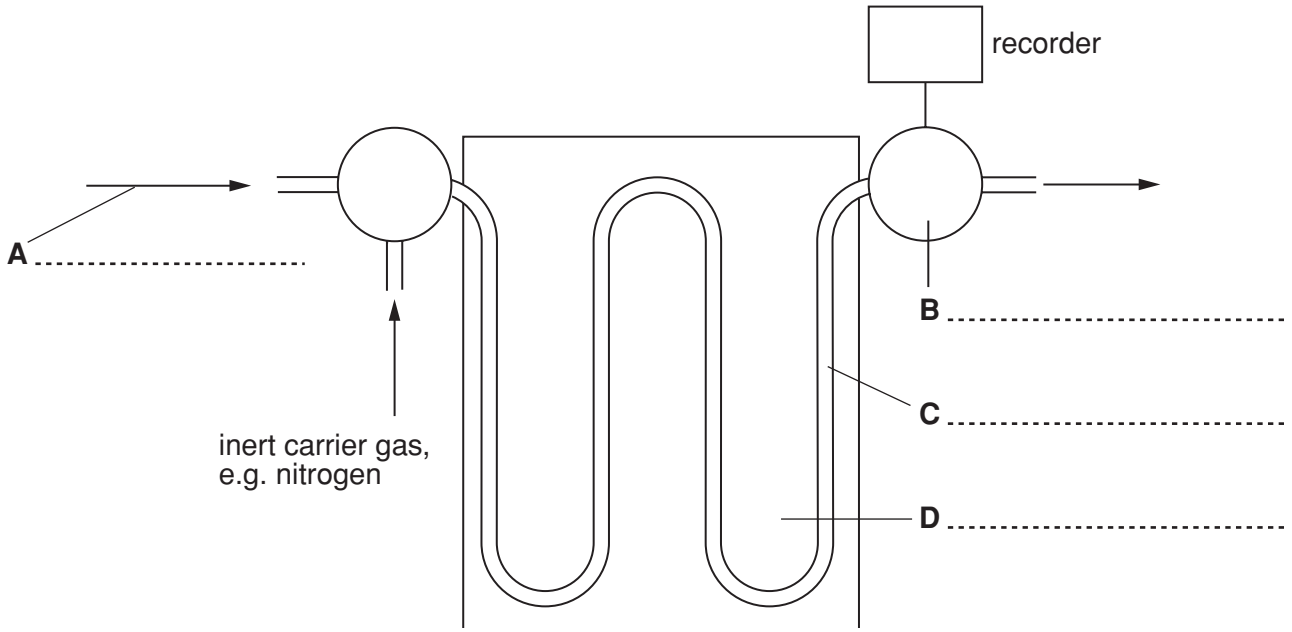
[Total: 31]

5 In 1982, King Henry VIII's flagship, the *Mary Rose*, was raised from the sea-bed where she had lain for 400 years. In the wreck was a medicine chest containing jars of ointment.

For Examiner's Use

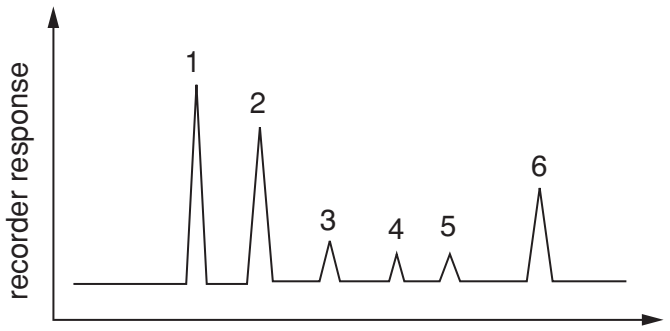
Archaeologists called in chemists to identify the ointment.

(a) The main technique used was gas-liquid chromatography.
A diagram of a gas-liquid chromatograph is shown below.
Complete the labels **A**–**D** by writing on the dotted lines.



[4]

(b) The recorder trace obtained from the ointment is shown below.



What is plotted on the horizontal axis?

.....[1]

[Turn over

(c) **(i)** Peak 1 was caused by hexadecanoic acid, a carboxylic acid with an unbranched chain containing sixteen carbon atoms.
Draw the skeletal formula for this acid.

For Examiner's Use

[2]

(ii) Another smaller peak is from an *unsaturated* acid. Name the functional group present in this compound which is **not** present in hexadecanoic acid.

.....[1]

(iii) Another peak was identified as 'triacontanol'. Explain how this name tells you that the compound contains an alcohol group.

.....

.....[1]

(iv) The substances in **(i)**, **(ii)** and **(iii)** came from the gradual breakdown of esters in beeswax. Circle in the list below the name of the process by which beeswax changed into these substances.

condensation elimination esterification hydrolysis reduction [1]

(d) Fats and oils are triesters of glycerol.
Draw the structure of the molecule formed when glycerol (propane-1,2,3-triol) reacts with three molecules of a long-chain carboxylic acid to form three ester links.

Use **full structural formulae** for the glycerol and ester parts of the molecule and **skeletal formulae** for the long chains of the carboxylic acids (the number of carbon atoms in the chain is not important).

[3]

[Total: 13]